The Purification of Mangrove Tannins

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Tannins of high purity may be obtained from the fresh mangrove extracts with high yield, utilising mixed solvent (acetone and methanol) purification technique. This method is much simpler and efficient as compared to other known methods.

Vegetable tannin extracts contain acids, salts, gums and sugars as nonphenolic nontannins and it is difficult to make the tannin completely free from these nontanins. It has been shown[1] that in most of the mangroves except goran (*Ceriops roxburghiana*) gums account for 20-30% of the weight of the extracts. Mangroves also contain high amount of salts, mainly salts of strong acids.[2] In the past, several methods have been suggested by a number of workers for the purification of tannins, mainly wattle tannins. Buchanan, Lewis and Weber[3] reported that it was not possible to prepare mangrove extracts of high purity. According to them, the solvent purification was not suitable for the purification of mangroves. They also reported that the mixtures of methanol and acetone or ethanol and acetone were no more effective than acetone alone in extracting the tannins from mangroves. Roux[4] reviewed exhaustively the previous work on the purification of tannins and came to the conclusion that none of the workers obtained tannins of high purity. Four methods were tried by him for the purification of wattle tannins—(i) hide powder method, (ii) lead salt method, (iii) salting out method and (iv) mixed solvent methods. He concluded that hide powder and lead salt methods are almost equally effective for obtaining tannin of about 95% purity. In a more recent paper, Roux *et al.*[5] stated that the lead salt method is the most satisfactory technique for obtaining pure wattle tannin of high yield from commercial mimosa extract. They improved the lead salt method by treating the lead tannate with charged Amberlite IR-120 resin and the tannins liberated were considered as very pure. But both the lead salt purification techniques were found to be unsuitable in the case of mangroves. The controlled mixed solvent purification technique was found to be very useful for the purification of mangrove tannins and good yield was obtained with ease. A mixture of methanol

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and acetone is found to be more effective than acetone alone for extracting the total tannins of mangroves.

Experimental

2 kg. fresh goran bark (*Ceriops roxburghiana*) was soaked with 4 times its weight of distilled water for two days at room temperature and the tan infusion was filtered through cotton wool. The bark residue was extracted in the same manner once more. The two consecutive extractions were then mixed and taken to complete dryness under reduced pressure.

100 g. of the dried extract was treated with 400 ml. of a mixture of acetone (analar) and methanol (analar) (3:1). The contents of the flask were then stirred for 5-10 minutes and then allowed to settle. The dissolved tannin was then filtered. The extract was again treated with acetone and methanol (120 ml.) in the same ratio as before and the dissolved tan solution was again filtered. The process was continued until the solution became almost colourless. The whole process of extraction was completed within 4-5 hours. The whole extract was then dried under vacuum and the dried powder was re-extracted with the mixture of acetone and methanol (5:1) in the same way as before and the extraction was completed within 2-3 hours. The extract was again dried and the dried product was finally purified with acetone and methanol (7:1) as in the previous procedure within one hour. The dried product was finally analysed and found to contain more than 90% tannin; the yield was 55 g.

For comparison, the water extract of goran (100 g.) was purified by the two lead salt purification methods.[4, 5] In the lead acetate purification process,[4] an attempt was made to extract the final product after neutralisation with dilute NaOH and drying under vacuum, first with acetone and then with alcohol. But the tannin was found to be very slightly soluble in both the solvents. It was then extracted with pure methanol. Tannins of about 85% purity was obtained. On following the more recent process suggested by Roux *et al*,[5] at the final stage after liberating the tannin from lead tannate with Amberlite resin IR-120 and filtering, centrifuging and drying, a good part of the tannin was found to be insoluble in water. All the tannin analyses were done by hide powder shake method. The analysis of all the extracts is given in table 1.

The water extract of the other species of fresh mangroves were also purified by changing the acetone and methanol ratio and repeating the purification procedure 3 or 4 times (e.g., in the case of *Bruguiera gymnorrhiza*, the ratio of acetone and methanol was kept 1:1 for the first purification, 3:1 for the second purification and 4:1 for the third purification) more than 90% purity was obtained.

Discussion

From the results, it is evident that of all the methods tried, the mixed solvent method is the best for the purification of mangrove tannins. The other two

methods suggested[4, 5] for the purification of wattle tannins were found to be not satisfactory for the purification of mangrove tannins. As the object was to prepare a bulk quantity of purified tannins, the hide powder method and salting out method were not tried.

It was shown by Cunningham and Ghosh[6] that lead acetate purification method[4] introduces some organic salt like sodium acetate in the tan liquor and suggested further purification of the tannins by dialysis. The yield by this procedure (42·9%) is much less as compared to the solvent purification. The second method suggested by Roux *et al.*[5] is also not applicable for the purification of mangrove tannins, as the solubility of the final product in water is very poor. More than 10% of the extract was found insoluble in water. The poor solubility of the mangrove tannins purified by this method might be due to very low pH (3·2) of the resulting tan solution which is presumably due to the liberation of acetic acid after treatment with charged Amberlite (cation exchange resin). At such a low pH the highly condensed tannin is likely to polymerise quickly making a part of the tannin insoluble in water. It has already been shown[7] that if a little more than 0·5 ml. acetic acid (2% solution) is added to 100 ml. fresh goran liquor (10° Bk), pH of the liquor goes down to 3·5-3·7 and a

Table 1

ANALYSIS OF THE ORIGINAL AND PURIFIED GORAN EXTRACTS ON MOISTURE FREE BASIS

	Goran (original)	Solvent purified	Lead acetate purifiefid	Lead acetate and Amberlite purified
Tannins %	70·8	92·3	85·8	72·5
Nontannins %	28·8	7·7	14·2	15·0
Insolubles %	0·4	—	—	12·5
T/NT	2·45	12·0	6·0	4·8
Yield (% on the weight of extract)	—	55·0	42·9	50·7
Yield (% on 70% tannin)	—	78·5	61·3	72·4
pH (analytical solution)	4·3	3·75	5·2	3·2
Total salt (sulphated ash method—(mg. eq. per 100 g. extract)	210·0	55·0	121·0	—
Salt of weak acid to pH 2·8 (mg. eq. per100 g.extract)	41·2	21·3	90·8	—
Total acidity to pH 5·8	21·2	25·6	3·8	—
Gums	6·8	nil	nil	nil
Sugars	trace	trace	trace	trace

part of the tannin get precipitated. The yield of the tannin by the above method is much more (50·7%) than that by the previous technique but much less than that by the mixed solvent purification technique.

From Table 1, it is obvious that salts and some acids are the major nontans in the purified extract, the lead acetate purified tannins containing the maximum amount of salts, mainly salts of weak acids. To make the tannins completely free from acids and salts electrodyalysis is deemed essential. Nevertheless, the possibility of getting tannins without any trace of acids and salts is doubtful.

The solvent purified tannins were found to be highly soluble in water and the yield was much more than in the other two methods. The procedure is very simple and the purified material can be obtained in bulk quantities.

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